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Termolecular Ion-Molecules Reactions in Titan's Atmosphere. I. Principal Ions with Principal Neutrals

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Abstract

The FA-SIFT experiment at Canterbury was used to determine some of the principal termolecular ion-molecule reactions that occur in Saturn's satellite Titan's atmosphere. The experiments were performed using both a pure nitrogen bath gas and a pure helium bath gas. The reactions of the ions N^+, N_2^+, N_3^+, N_4^+, $HCNH^+$, c-$C_3H_3^+$, and H_3O^+ with molecular nitrogen were studied in a nitrogen bath gas at room temperature. Only two of these ions, N^+ and N_2^+ were observed to react with N_2 forming N_3^+ and N_4^+ respectively. A second set of experiments were performed that measured the reactivity of ions in Titan's atmosphere that do not undergo rapid bimolecular reactions with other species. The reactions of these so-called "terminal" ions ($HCNH^+$, c-$C_3H_3^+$ and H_3O^+) with the trace neutral constituents of Titan (CH_4, C_2H_2 and C_2H_4) were also examined using both helium and nitrogen as the bath gas. The only reactions observed to occur were the termolecular reactions of $HCNH^+$ and H_3O^+ with C_2H_2, and C_2H_4. Finally, a third set of reactions were studied. These were the reactions of N_3^+ and N_4^+ with the species CH_4, C_2H_2, C_2H_4, HCN, and C_4H_8. All of the reactions in this third set have bimolecular ion-molecule kinetics and they are compared in the text with the similar reactions of N^+ and N_2^+ with these reagents.

Introduction

On October 15th of 1997 a Titan IVB rocket launched a payload from the Earth and projected it on an interplanetary course that will take it eventually into an orbit around the planet Saturn.[1,2] The payload was the Cassini space craft with a special Titan probe named after the astronomer Huygens. During orbit around Saturn the spacecraft will use the gravity of the Saturnian satellite Titan to alter its trajectory, thereby facilitating a comprehensive exploration of Saturn and its moons. This procedure requires the spacecraft to fly through the ionosphere of Titan many times.

Titan has been explored previously by the pair of Voyager spacecraft using remote optical spectroscopy[3-5] and also radio occultations.[6,7] Titan has also been studied using Earth-based astronomical telescopes. These studies show that Titan has the most extensive atmosphere of any planetary satellite in our solar system. While Titan is much less massive than Earth it has a larger atmospheric pressure at its surface (~ 1.6 Bar). Compared with Earth, the atmosphere of Titan has a greater depth due to the smaller mass of this satellite. Titan's atmosphere consists mainly of nitrogen gas (94%) with the remaining 6% of the atmosphere consisting of the hydrocarbon gases: methane, acetylene, ethylene and ethane.[8,9]

A quadrupole mass spectrometer on the Cassini spacecraft will sample the neutrals and ions present in Titan's ionosphere.[10] It is therefore necessary to gain an understanding of the ion chemistry that might occur in such an environment. Many of the pertinent bimolecular ion-molecule reactions relevant to Titan's unusual atmospheric composition have previously been characterised.[11]

The atmosphere of Titan is a unique chemical mix of nitrogen and hydrocarbons. The chemical processing that occurs produces a most interesting selection of chemical species, that can be described as a soup of both interesting and exotic molecules. The chemical processing occurs by both heterogeneous reactions and homogeneous gas phase reactions involving both ion and neutral chemistry. Ion-neutral reactions that have been studied show how some of the processing can take place. Of particular interest is how N_2 is incorporated into hydrocarbon species. Although molecular nitrogen is unreactive to almost all ions it has been found that the N^+ and N_2^+ ions do undergo a range of reactions with hydrocarbons in

which some of the products are nitrile ions. These nitrile ions in turn react with further hydrocarbons forming larger nitriles.

Earlier inosopheric studies have been primarily concerned with the lower pressure, upper photo-ionosphere of Titan, in which bimolecular kinetics predominate. At the lower limit of Titan's photo-ionosphere the pressure is sufficient to make fast termolecular reactions competitive with the bimolecular reactions. A knowledge of active termolecular chemistry therefore should be of interest to the planetary community, particularly at Titan altitudes of less than 900 km. Several ion-neutral association reactions have been observed in the laboratory occurring in hydrocarbon ion-nitrile reactions[12-21]. Termolecular rate coefficients have been measured for several of these ion-association reactions in the past and some were found with very large rate coefficients $k_{assoc} \sim 10^{-23}$ cm^6 s^{-1}. Ion association reactions that are this fast can compete efficiently with bimolecular channels at altitudes corresponding to the lower photo-ionosphere of Titan.

We describe here a systematic study of the termolecular ion-molecules reactions that are occurring in Titan's atmosphere in a nitrogen atmosphere of 0.5 Torr and above.

Experimental

The results presented in this work were obtained using the University of Canterbury's flowing afterglow-selected ion flow/drift tube (FA-SIFDT). The SIFT technique and this apparatus have been described elsewhere so only a short discussion of the basic principles of operation will be discussed here.[22] The Canterbury FA-SIFDT uses a flowing afterglow (FA) section as an ion source. This ion source can operate in conjunction with different ionization methods: the method of choice being that which produces the ion of interest most efficiently. The N_3^+ and N_4^+ ions were formed by using a microwave discharge on a nitrogen carrier gas thus generating N^+ and N_2^+ ions. The ensuing reactions of these ions with N_2 in the FA generated N_3^+ and N_4^+ respectively. The other ions were formed by adding appropriate source gases to either a helium or hydrogen afterglow in the FA source. It was found that photoionisation of the bath gas in the reaction tube could cause problems when reactions with N_2 as the

third body were being evaluated. Consequently for these reactions, either an off-axis discharge with a Wood's Horn to trap photons, or an electron impact type ion source was used.

All measurements are reported at 295±5K and the bimolecular rate coefficients were obtained at 0.47 Torr. The termolecular measurements were made over a range of pressure from about 0.2 Torr to 0.7 Torr for the rate coefficients measured in helium, and about 0.1 Torr to 0.6 Torr, for the rate coefficients measured in a nitrogen carrier gas. The highest pressures in each case were obtained through 'throttling' of the roots blower connected to the main flow tube. In effect we extended the available pressure range of the mass flow controllers by conductance limiting the flow speed in the reaction tube with the result of a higher pressure in the flow tube for a specific through-put of gas.

The gases used were mostly obtained from commercial sources and purified by multiple freeze-pump-thaw cycles. Hydrogen cyanide was an exception, being prepared by the action of sulfuric acid on KCN. The nitrogen used as a carrier gas was zero-grade (99.998% pure) and was further scrubbed by passage through a molecular sieve trap immersed in a dry ice/acetone mix to remove as much water impurity as possible. The helium used as a carrier was instrument grade (99.99% pure) and was further scrubbed by passage through a molecular sieve trap immersed in liquid nitrogen to remove as many condensable impurities as possible. The bimolecular ion-molecule reaction rate coefficients are estimated to have uncertainties of ±20% and the termolecular ion-molecule reaction rate coefficients are estimate to have uncertainties of ±30%.

Thermochemical heats of formation of the ions and neutrals used in the calculation of the heats of reactions, were taken from the standard NIST tables. [23]

Results

A summary of the results of this investigation are shown in Tables 1 and 2.

The two ions, N_3^+ and N_4^+, were derived from a nitrogen afterglow and are likely to have bound deep well structures that are 3.74 eV (361 kJ mol^{-1})[24] and 1.09 eV (106 kJ mol^{-1})[25] respectively below the $N^+ + N_2$ and $N_2^+ + N_2$ entrance energies. Both reactions leading to the formation of N_3^+ and N_4^+

have been measured previously and are slow (N_3^+,[26,27] N_4^+ [27-34]) which is somewhat surprising in view of the relatively deep wells between reactants and product.

$$N^+ + N_2 + N_2 \rightarrow N_3^+ + N_2 \quad (1)$$

$$k = 4.0 \times 10^{-29}\ cm^6\ s^{-1}\ (M = N_2)\ [27]$$

$$N_2^+ + N_2 + N_2 \rightarrow N_4^+ + N_2 \quad (2)$$

$$k = 8.0 \times 10^{-29}\ cm^6\ s^{-1}\ (M = N_2)\ [27]$$

Our measured values for these two reactions with *helium* as the bath gas are $k = 2 \times 10^{-29}$ cm^6 s^{-1} (reaction 1) and $k = \geq 2 \times 10^{-29}$ cm^6 s^{-1} (reaction 2). However, the low association rates are the consequence of having a small number of internal modes available for energy dissipation within the complex. Association reactions are strongly temperature dependent and the temperature dependence has been measured for reaction (2).[34] At a temperature of 135 K corresponding to the lower ionosphere of Titan, the rate coefficient for reaction (2) increases to 3×10^{-28} cm^6 s^{-1}.[34]

N_3^+ and N_4^+ reactions

Both ions, N_3^+ and N_4^+ could be readily injected from the FA source region of the FA/SIFDT instrument after mass selection, into the reaction tube. The reactions of these ions with the main minor constituents of Titan's atmosphere, (CH_4, C_2H_2 and C_2H_4) were examined as also were their reactions with HCN and C_4H_8 in a helium buffer gas.

Each N_n^+ ion exhibited bimolecular reactions with these reactants. There was however, a notable distinction between the reactions of N_3^+ and N_4^+. Whereas N_4^+ exhibited mainly charge transfer and dissociative charge transfer reactions, N_3^+ transferred N^+ to the reactant neutral. In the discussions that follow, although the reactions exhibit bimolecular kinetics we have included the helium bath gas in the equation merely to emphasize the environment in which the reactions were studied. The nature of the bath gas is not expected to influence reactions exhibiting bimolecular kinetics in any way. There is some ambiguity in the literature as to the structure of the N_4^+ ion. Two structures are possible contenders for the ion in this study: a linear structure or a non-planar Z-shaped structure.[35] N_2^+-N_2 energies calculated using ab-initio methods show the Z-shaped structure to be the most stable isomer.[35,36] However,

estimated binding energies for the linear structure match the measured N_4^+ binding energy most closely.[25] ESR studies of N_4^+ in a neon matrix at 4 K also indicate a linear structure.[37]

N_3^+ reactions

CH_4

Two product channels were observed in this reaction:

$$N_3^+ + CH_4 + He \xrightarrow{\sim 0.95} H_2CN^+ + N_2 + H_2 + He + 487 \text{ kJ mol}^{-1} \quad (3a)$$

$$\xrightarrow{\sim 0.05} CH_2NH_2^+ + N_2 + He + 672 \text{ J mol}^{-1} \quad (3b)$$

$$k_3 = 5.8 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$$

The exothermicity for each channel is assigned on the basis that the ion structures are $HCNH^+$ (reaction (3a)) and $CH_2NH_2^+$ (reaction 3b). Each channel is very exoergic and the small rate coefficient being much less than the Langevin capture rate ($k_L = 1.1 \times 10^{-9}$ cm^3 s^{-1}) may be indicative of a barrier on the potential surface.

C_2H_2 and C_2H_4

$$N_3^+ + C_2H_2 + He \xrightarrow{0.90} CH_2CN^+ + N_2 + He + 541 \text{ kJ mol}^{-1} \quad (4a)$$

$$\xrightarrow{0.05} C_2N^+ + H_2 + N_2 + He + 121 \text{ kJ mol}^{-1} \quad (4b)$$

$$\xrightarrow{0.05} HCNH^+ + C + N_2 + He + 72 \text{ kJ mol}^{-1} \quad (4c)$$

$$k_4 = 1.2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$$

The major channel (4a) is very exoergic and proceeds efficiently via N^+ transfer at the Langevin collision rate ($k_L = 1.1 \times 10^{-9}$ cm^3 s^{-1}) thereby incorporating nitrogen into the hydrocarbon ion.

$$N_3^+ + C_2H_4 + He \rightarrow C_2H_4^+ + N + N_2 + He + 27\ kJ\ mol^{-1} \quad (5)$$

$$k_5 = 1.1 \times 10^{-9}\ cm^3\ s^{-1}$$

The reaction with ethylene is not as exoergic as the preceding reactions of N_3^+ and few product channels are available for reaction with only charge transfer occurring at the collision rate ($k_L = 1.2 \times 10^{-9}\ cm^3\ s^{-1}$). The $C_2H_4^+$ product was confirmed by using deuterated ethylene.

HCN

$$N_3^+ + HCN + He \rightarrow HCN_2^+ + N_2 + He \quad (6)$$

$$k_6 = 6.7 \times 10^{--10}\ cm^3\ s^{-1}$$

The product of the reaction with HCN is unusual in that it does not appear to have been reported previously and its structure is unknown. It is plausible that an azide type structure is involved which raises the intriguing prospect of potentially interesting trace molecules in Titan's atmosphere. The efficient formation of HCN_2^+ implies the product ion has a stable structure with $\Delta H_f(HCN_2^+) < 1176$ kJ mol^{-1}.

C_4H_8

$$N_3^+ + C_4H_8 + He \rightarrow C_4H_8 + He + 168\ kJ\ mol^{-1} \quad (7)$$

$$k_7 = 1.3 \times 10^{-9}\ cm^3\ s^{-1}$$

The reaction of N_3^+ with 2-butene occurs at the collision rate ($k_L = x\ 10^{-9}\ cm^3\ s^{-1}$) via a simple charge transfer reaction.

N_4^+ reactions

As mentioned previously, N_4^+ exhibited charge transfer and dissociative charge transfer reactions with the hydrocarbons examined and also with HCN. All reactions occur at close to their collision rates (see Table 1) and are exoergic as follows: the reaction with CH_4, by 182 kJ mol^{-1}; C_2H_2 by 298 kJ mol^{-1};

C_2H_4 by 384 kJ mol^{-1}; C_4H_8 by 520 kJ mol^{-1} for the $C_4H_8^+$ ion product channel and 298 kJ mol^{-1} for the $C_3H_5^+$ (allene structure assumed) ion product channel; HCN by 86 kJ mol^{-1}.[23]

Association Reactions

Association with N_2

In the reactions included here (Table (2), the buffer gas is either helium or nitrogen.

None of the "terminal" ions that appear unreactive in Titan's atmosphere, *viz.* $HCNH^+$, c-$C_3H_3^+$ and H_3O^+ exhibited association with nitrogen under room temperature conditions.

$HCNH^+$ reactions with aliphatic hydrocarbons

Slow association was observed to occur with C_2H_2 and C_2H_4 but not with CH_4.

$$HCNH^+ + C_2H_2 + He, N_2 \rightarrow HCNH^+(C_2H_2 + He, N_2 \quad (8)$$

$k = 6 \times 10^{-29}$ cm^6 s^{-1} (M = He) and $k = 4 \times 10^{-28}$ cm^6 s^{-1} (M = N_2).

This reaction was also measured by Herbst *et al.*[34] who reported a value of $k = 5 \times 10^{-29}$ cm^6 s^{-1} at 300 K and 1.5×10^{-28} cm^6 s^{-1} at 210 K (M = He). The structure of the association ion $C_3H_4N^+$ is uncertain. Herbst et al. have argued that the product ion is unlikely to be protonated acrylonitrile, CH_2CHCNH^+, on the grounds that the calculated association rate assuming the CH_2CHCNH^+ structure, is larger than the experimental value by several orders of magnitude.[38] However, a strongly bound structure might be possible if the association mechanism does not conform to the simple model for association assumed by Herbst *et al.* Alternatively, a more weakly bound electrostatic complex may be a candidate for the structure of the product association ion.

$$HCNH^+ + C_2H_4 + He, N_2 \rightarrow HCNH^+ \bullet C_2H_4 + He, N_2 \quad (9)$$

$k = 5 \times 10^{-27}$ cm^6 s^{-1} (M = He) and $k = 1 \times 10^{-26}$ cm^6 s^{-1} (M = N_2).

An earlier measurement by Herbst *et al.*[38] reported (M = He) $k = 7 \times 10^{-27}$ cm^6 s^{-1} at 300 K and 1.8×10^{26} cm^6 s^{-1} at 210 K. A very similar situation exists in this reaction as in reaction (8) when the question

of association product ion structure identification is considered. Again the calculated association rate assuming the association product ion has the protonated propane nitrile structure, $C_2H_5CNH^+$, is too large and other less stable isomers are more likely.[38] The protonated propane isonitrile, $C_2H_5NCH^+$, is one possibility.

c-$C_3H_3^+$ ions did not exhibit association with any of the hydrocarbon molecules CH_4, C_2H_2 or C_2H_4.

H_3O^+ ion. No association was observed with CH_4. Association products were found for the reactions with C_2H_2 and C_2H_4.

$$H_3O^+ + C_2H_2 + He, N_2 \rightarrow H_3O^+\bullet C_2H_2 + He, N_2 \qquad (10)$$

$$k = 7 \times 10^{-28} m^6 s^{-1} (M = He) \text{ and } k = 9 \times 10^{-27} cm^6 s^{-1} (M = N_2)$$

Herbst *et al.*[34] reported termolecular rate coefficient for reaction (10) (M = He) of $k = 8 \times 10^{-28}$ cm^6 s^{-1} at 300 K and $k = 2.5 \times 10^{-27}$ cm^6 s^{-1} at 210 K. Fairley *et al.*[39] have examined the ion structure of the $C_2H_5O^+$ association product ion in reaction (11a) and have concluded that it is a 50/50 mixture of protonated vinyl alcohol, $CH_2CHOH_2^+$ and either protonated acetaldehyde CH_3CHOH^+ or the electrostatic complex $H_3O^+C_2H_2$. Subsequent experiments in this laboratory have since shown the ratio of vinyl alcohol to be closer to 75% and that the electrostatic complex is most likely responsible for the remaining 25%.[40]

$$H_3O^+ + C_2H_4 + He, N_2 \rightarrow H_3O^+\bullet C_2H_4 + He, N_2 \qquad (11a)$$

$$k_{10a} = 2 \times 10^{-27} cm^6 s^{-1} (M = He) \text{ and } 2 \times 10^{-26} cm^6 s^{-1} (M = N_2)$$

$$\rightarrow C_2H_5^+ + H_2O + He, N_2 \qquad (11b)$$

$$k_{10b} = 5.9 \times 10^{-11} cm^3 s^{-1}$$

For this reaction Herbst *et al.*[34] report a rate coefficient (M = He) $k = 7 \times 10^{-27}$ cm^6 s^{-1} at 300 K and $k = 1.8 \times 10^{-26}$ cm^6 s^{-1} at 210 K. Fairley *et al.*[41] and Matthews *et al.*[42] examined the structure of the association product ion and concluded it has the protonated ethanol, $C_2H_5OH_2^+$ structure.

Concluding Remarks

Whereas previous studies of ion molecule reactions in Titan's ionosphere have been mainly concerned with bimolecular kinetics the association experiments reported here were undertaken to assess the importance of termolecular ion chemistry. The experiments were performed with a nitrogen as well as helium buffer gas in order to simulate more closely the atmosphere of Titan. The working pressure of the flow tube, 0.5 Torr, corresponds in pressure to an altitude on Titan of 230 km. We have used the rate coefficients reported here and the model of Yelle giving the variation in temperature and number density of Titan's atmosphere[43] to derive the relative amounts of N^+, N_2^+, N_3^+ and N_4^+ as a function of altitude of Titan and these are shown in Figure 1.

Above about 200 km, ionization of N_2, viz. N^+ and N_2^+, represent the source of over 90% of all the positive ions in Titan's atmosphere. Below 200 km (equivalent to Titan's stratosphere) these ions are converted into N_3^+ and N_4^+ by reactions (1) and (2). It is in this region that the reactions of N_3^+ and N_4^+ ions (initiated by cosmic ray ionization) shown in Table 1 become significant. The principal loss process for N_4^+ is reaction with CH_4. The N_3^+ ion also reacts with CH_4, but with a rate coefficient that is much smaller than the collision rate. The much faster reaction of N_3^+ with C_2H_2 therefore becomes competitive.

It is also apparent from the reactions listed in Table 2 that the cyclopropyl ion, c-$C_3H_3^+$, designated as a "terminal" ion in our earlier review of the ion chemistry of Titan,[11] remains unreactive to termolecular loss with all neutral reactants examined. As our knowledge stands at present, there are no efficient ion-molecule exchange processes for c-$C_3H_3^+$ in Titan's ionosphere. The loss process of c-$C_3H_3^+$ with C_4H_2 shown in our review[11] was incorrect. c$C_3H_3^+$ will be lost only through electron recombination.

The addition of the termolecular loss processes for $HCNH^+$ shown in Table 2 begin to become important when compared to electron ion recombination below about 600 km. The identity of the structure of the association product ions of $HCNH^+$ still remains unanswered but nitriles or isonitriles ions are plausible possibilities.

Termolecular association of H_3O^+ with the hydrocarbons C_2H_2 and C_2H_4 becomes larger than electron ion recombination below about 550 km forming protonated vinyl alcohol and possibly acetaldehyde and protonated ethanol.

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Figure Caption

Figure 1 Variation in relative amounts of N^+ (■), N_2^+ (a), N_3^+ (▲) and N_4^+ (d) with altitude.

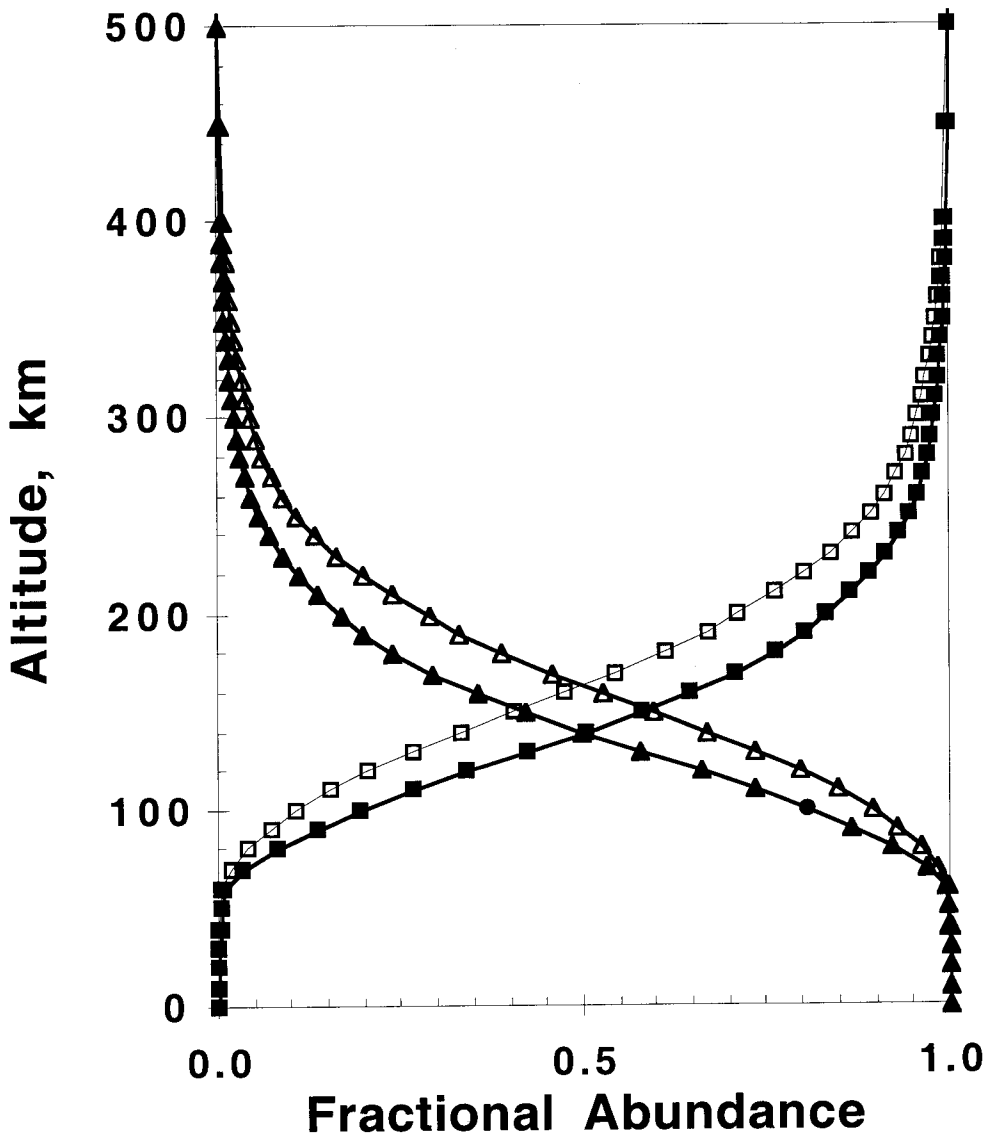

Table 1.Reactions measured in this study relating to the formation and loss of N_3^+ and N_4^+ ions.

Reactants			Branching Ratio	Products[a]				k[b]	ΔH°/ kJ mol^{-1} [c]
N^+	+ N_2	+ N_2	1.0	N_3^+		+ N_2	+ N_2	4.0×10^{-29} [d]	
N_2^+	+ N_2	+ N_2	1.0	N_4^+		+ N_2	+ N_2	8.0×10^{-29} [d]	
N_3^+	+ CH_4	+ He	~0.95	$HCNH^+$	+ H_2	+ N_2	+ He	5.8×10^{-11}	-487
			~0.05	$CH_2NH_2^+$		+ N_2	+ He		-673
N_3^+	+ C_2H_2	+ He	0.90	CH_2CN^+		+ N_2	+ He	1.2×10^{-9}	-541
			0.05	C_2N^+	+ H_2	+ N_2	+ He		-121
			0.05	$HCNH^+$	+ C	+ N_2	+ He		-72
N_3^+	+ C_2H_4	+ He	1.0	$C_2H_4^+$	+ N	+ N_2	+ He	1.1×10^{-9}	-27
N_3^+	+ C_2D_4	+ He	1.0	$C_2D_4^+$	+ N	+ N_2	+ He	9.9×10^{-10}	-27
N_3^+	+ HCN	+ He	1.0	HCN_2^+		+ N_2	+ He	6.7×10^{-10}	
N_3^+	+ C_4H_8	+ He	1.0	$C_4H_8^+$	+ N	+ N_2	+ He	1.3×10^{-9}	-163
N_4^+	+ CH_4	+ He	1.0	CH_4^+		+ 2 N_2	+ He	1.1×10^{-9}	-182
N_4^+	+ C_2H_2	+ He	1.0	$C_2H_2^+$		+ 2 N_2	+ He	9.2×10^{-10}	-298
N_4^+	+ C_2H_4	+ He	1.0	$C_2H_4^+$		+ 2 N_2	+ He	$\sim 1.1 \times 10^{-9}$	-384
N_4^+	+ C_2D_4	+ He	1.0	$C_2D_4^+$		+ 2 N_2	+ He	1.1×10^{-9}	-384
N_4^+	+ HCN	+ He	1.0	HCN^+		+ 2 N_2	+ He	2.6×10^{-9}	-86
N_4^+	+ C_4H_8	+ He	[e]	$C_4H_8^+$		+ 2 N_2	+ He	$\sim 1.1 \times 10^{-9}$	-520
			[e]	$C_3H_5^+$	+ CH_3	+ 2 N_2	+ He		-298

a) Most of the reactions in this Table have bimolecular kinetics and their rate coefficient is thus independent on the nature of the bath gas. The bath gas has only been shown in the equation to emphasise that these reactions were measured under similar conditions of pressure as those existing in Titan's lower ionosphere.

b) Units are $cm^6\ s^{-1}$ for termolecular reactions and $cm^3\ s^{-1}$ for bimolecular reactions.

c) Ref. 23.

d) From ref. 27 for M = N_2. Our measured results are (M = He) 2×10^{-29} $cm^6\ s^{-1}$ (N^+), $\geq 2 \times 10^{-29}$ $cm^6\ s^{-1}$ (N_2^+).

e) Absolute rate coefficients and branching ratios could not be measured due to the mass coincidence at m/e = 56^+.

Table 2.Association reactions measured in this study.

Reactants	Association Product	Bath Gas	Rate Coefficient
$HCNH^+ + 2\ N_2$	No Reaction		
$c\text{-}C_3H_3^+ + 2\ N_2$	No Reaction		
$H_3O^+ + 2\ N_2$	No Reaction		
$HCNH^+ + CH_4 + M$	No Reaction		$\leq 1 \times 10^{-13}$ [a] M=He & N_2
$HCNH^+ + C_2H_2 + He$	$HCNH^+ \bullet C_2H_2$	+ He	6×10^{-29} [b]
$HCNH^+ + C_2H_2 + N_2$	$HCNH^+ \bullet C_2H_2$	+ N_2	4×10^{-28} [b]
$HCNH^+ + C_2H_4 + He$	$HCNH^+ \bullet C_2H_4$	+ He	5×10^{-27} [b]
$HCNH^+ + C_2H_4 + N_2$	$HCNH^+ \bullet C_2H_4$	+ N_2	1×10^{-26} [b]
$c\text{-}C_3H_3^+ + CH_4 + M$	No Reaction		$\leq 1 \times 10^{-11}$ [a] M=He & N_2
$c\text{-}C_3H_3^+ + C_2H_2 + M$	No Reaction		$\leq 1 \times 10^{-13}$ [a] M=He & N_2
$c\text{-}C_3H_3^+ + C_2H_4 + M$	No Reaction		$\leq 1 \times 10^{-13}$ [a] M=He & N_2
$H_3O^+ + CH_4 + M$	No Reaction		$\leq 5 \times 10^{-13}$ [a] M=He & N_2
$H_3O^+ + C_2H_2 + He$	$H_3O^+ \bullet C_2H_2$	+ He	7×10^{-28} [b]
$H_3O^+ + C_2H_2 + N_2$	$H_3O^+ \bullet C_2H_2$	+ N_2	$\sim 9 \times 10^{-27}$ [b]
$H_3O^+ + C_2H_4 + He$	$H_3O^+ \bullet C_2H_4$	+ He	2×10^{-27} [b]
$H_3O^+ + C_2H_4 + N_2$	$H_3O^+ \bullet C_2H_4$	+ N_2	2×10^{-26} [b]

[a] Rate coefficient limit expressed for a pseudo second order reactions of $cm^3\ s^{-1}$.

[b] Termolecular rate coefficient in units of $cm^6\ s^{-1}$.